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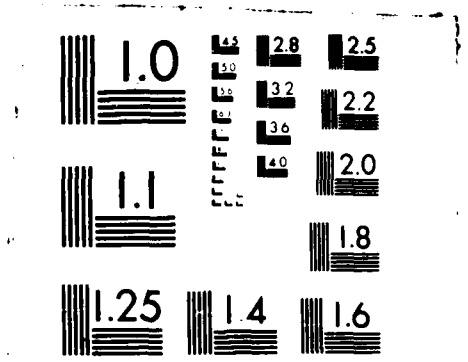

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This report summarizes work completed under grant AFOSR-86-0006. It involves both theoretical and experimental papers which were published recently, and the theoretical work focuses on novel approaches to control of selectivity of photochemical reactions.

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FINAL REPORT

AFOSR-86-0006

THEORETICAL AND EXPERIMENTAL STUDIES OF MOLECULAR DYNAMICS

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JANUARY 1987

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January 2, 1987

Ms. Wilson
Department of the Air Force
Air Force Office of Scientific Research
Bolling Air Force Base, D.C. 20332-6448

Dear Ms. Wilson

This letter contains the final report for grant AFOSR-86-0006 - 49620.

During the period of October 1, 1985 through September 30, 1986, the work described in the following papers was completed.

Selectivity of Elementary Molecular Processes Associated with Energy Transfer and Chemical Reaction, S.A. Rice, J. Phys. Chem. **90**, 3063 (1986).

This paper contains a review of experimental and theoretical work concerned with the selectivity of collision induced vibrational relaxation and proposes a new method for achieving selectivity of chemical reactivity.

Fractal Behavior in Classical Collisional Energy Transfer. D.W. Noid, Stephen K. Gray and Stuart A. Rice, J. Chem. Phys. **84**, 2649 (1986).

A plot of final vibrational action vs. initial vibrational phase for a two-degree of freedom model for He + I_2 collisions is examined and shown to exhibit a chattering region. The chattering region is shown to exhibit a very intricate structure, including an infinite number of regions of regularity which we term icicles. Structure is evident on all scales of examination and a fractal dimension close to 2 is obtained for some regions of the chattering region. The survival probability associated with the complexes shows an initial fast decay, due to the icicles, but can be roughly characterized over a longer and wider time range by a more slowly decaying

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exponential.

Bottlenecks to Unimolecular Reactions and an Alternative Form for Classical RRKM Theory. J. Phys. Chem. **90**, 3470 (1986). Stephen K. Gray, Stuart A. Rice and Michael J. Davis

Bottlenecks to the flow of phase points in the classical phase space of a triatomic molecule are discussed and approximated for the example of van der Waals predissociation of HeI_2 . An alternative form for the usual transition state theory of unimolecular reactions, RRKM theory, is developed by approximating the intermolecular (separatrix) bottleneck and using it as a basis for the transition state surface. The rates obtained with the theory are in surprisingly good accord with dynamical rates from classical trajectory studies.

Coherent Pulse Sequence Induced Control of Selectivity of Reactions: Exact Quantum Mechanical Calculations. J. Chem. Phys. **85**, 5805 (1986). David J. Tannor, Ronnie Kosloff and Stuart A. Rice.

We present a novel approach to the control of selectivity of photochemical reaction products. The central idea is that in a two-photon or multiphoton process that is resonant with an excited electronic state, the resonant excited state potential energy surface can be used to assist chemistry on the ground state potential energy surface. By controlling the delay between a pair of ultrashort (femtosecond) laser pulses, it is possible to control the propagation time on the excited state potential energy surface. Different propagation times, in turn, can be used to generate different photochemical products. There are many cases for which selectivity of product formation should be possible using this scheme. Our examples show a variety of behaviors ranging from virtually 100% selectivity to poor selectivity, depending on the nature of the excited state potential energy surface. Branching ratios obtained using a swarm of classical trajectories are in good qualitative agreement with full quantum mechanical calculations.

Photon Echos in Multilevel Systems. In "Understanding Molecular Properties", D. Reidel Publisher, April 1986. David J. Tannor and Stuart A. Rice

We describe, via a study of the photon echo phenomenon, both formal and conceptual bridges between the strong field behavior of two-level systems and of two electronic state systems in the Born-Oppenheimer representation. The multiplicity of vibrational levels characteristic of the latter is taken into account implicitly via the description of wavepacket propagation on each of the two potential surfaces. Various coherent optical effects are examined. Wavepacket motion on the excited Born-Oppenheimer surface leads to free induction

decay. A π-pulse exchanges the wavepackets of the two potential surfaces, subject to a constraint defined by the Franck-Condon principle. A photon echo results when and if the excited electronic state wavefunction and ground electronic state wavefunction overlap.

The Photofragmentation of Simple Van der Waals Complexes: Classical Statistical Theory and Comparison with Exact Classical and Approximate Quantum Dynamics Results. Faraday Disc. #82, September 1986. Stephen K. Gray and Stuart A. Rice.

A recently proposed statistical theory for unimolecular reactions, based on employing approximate phase space bottlenecks as transition states, is discussed and a new and simpler expression for the rate constant is derived. The theory is applied to a collinear model of van der Waals molecule fragmentation and the results are compared with exact classical and approximate quantum mechanical rate constants. Sources of nonstatistical behavior and classical/quantum mechanical disrepancy are discussed.

Lifetimes of Degenerate Benzene $^1B_{2u}$ Levels Split by Vibrational Angular Momentum. J. Chem. Phys. (in press). Ron L. Rosman, Albert A. Villaeys, Karl F. Freed, and Stuart A. Rice

This work examines, both experimentally and theoretically, the lifetimes of nominally degenerate benzene $^1B_{2u}$ levels split by differential coupling of the vibrational angular momentum components. We report fluorescence lifetimes for the 6^116^2, 6^110^2, and 6^117^2 levels of the S_1 electronic state in cold C_6D_6 in a supersonic jet. The higher energy vibrational angular momentum component has the longer lifetime. Calculations of the nonradiative decay rates for these levels are presented. Calculations based on conventional radiationless transition theory, assuming the prepared state is a single vibronic level, are not able to explain the experimental results, and we conclude that another mechanism must be responsible for the observed lifetime differences. We present a qualitative explanation of the data that takes into account perturbations of zeroth-order harmonic oscillator states by cubic and quartic vibrational anharmonicities and by Coriolis coupling. These perturbations affect the split vibrational angular momentum components differently and are capable of producing differences in lifetimes.

Fluorescence Lifetimes of Mode 6^1 in Deuterobenzenes: Fine Structure in the Decay Lifetime Spectrum. Chem. Phys. Letts. 132, 351 (1986). Ron L. Rosman and Stuart A. Rice

We report measurements of the fluorescence lifetimes of vibrational level 6^1 in the first excited singlet state of several deuterobenzenes. In the lower symmetry compounds, where $6a^1$ and $6b^1$ are not degenerate, the higher energy level always has the longer fluorescence lifetime. This observation is consistent with the results of earlier studies of the lifetimes of nominally degenerate benzene vibrational levels. Using perturbation theory arguments, we suggest a physically plausible explanation which can account for the higher-lying component of a pair of split levels having the longer lifetime.

Intramolecular Vibrational Energy Relaxation Induced by van der Waals Molecule Fragmentation: The Systems $C_6H_{6-n}D_n \cdot He_{1,2}$. J. Chem. Phys. (in press). Ron L. Rosman and Stuart A. Rice

We report the results of experiments which probe the vibrational energy redistribution which accompanies fragmentation of deuterobenzene-helium van der Waals molecules. Branching ratios for vibrational relaxation to various final states were obtained for initially prepared levels 6^1-$He_{1,2}$, $6^1 16^2$-He_1, $11^1 17^1$-He_1, and 17^2-He_1 in several deuterobenzene compounds. The probabilities of transitions to final states in the relaxation from 6^1-He_1 show general agreement with an energy gap law, and relaxation from $6^1 16^2$-He_1, $11^1 17^1$-He_1, and 17^2-He_1 favors small vibrational quantum number changes. The experiments were undertaken to illuminate how molecular symmetry influences the choice of pathways for vibrational energy redistribution associated with van der Waals molecule predissociation. The data for the various $C_6H_{6-n}D_n \cdot He_{1,2}$ systems, however, show very different relaxation patterns. These patterns can not readily be explained by the usual intramolecular vibrational coupling mechanisms.

Phase Space Bottlenecks and Statistical Theories of Isomerization Reactions. J. Chem. Phys. (in press). Stephen K. Gray and Stuart A. Rice.

We examine the dynamics of isomerization reactions and point out the existence of important phase space bottlenecks. A three-state statistical theory based on the behavior of trajectories and the properties of the phase space bottlenecks is proposed; this theory is better than standard two-state RRKM theory under some circumstances and offers a new way of conceptualizing isomerization. We test our ideas on the simple system, consisting of an equivalent double well coupled to a Morse oscillator, which was studied by DeLeon and Berne. Approximate methods of obtaining the required elementary rate constants in our theory are also discussed.

Coherent Pulse Sequence Induced Control of Selectivity of Reactions: Exact Quantum Mechanical Calculations. J. Chem. Soc. Faraday 2, in press. David J. Tannor, Ronnie Kosloff and Stuart A. Rice.

We present a novel approach to the control of selectivity of photochemical reaction products. The central idea is that in a two-photon or multiphoton process that is resonant with an excited electronic state, the resonant excited state potential energy surface can be used to assist chemistry on the ground state potential energy surface. By controlling the delay between a pair of ultrashort (femtosecond) laser pulses, it is possible to control the propagation time on the excited state potential energy surface. Different propagation times, in turn, can be used to generate different photochemical products. There are many cases for which selectivity of product formation should be possible using this scheme. Our examples show a variety of behaviors ranging from virtually 100% selectivity to poor selectivity, depending on the nature of the excited state potential energy surface. Branching ratios obtained using a swarm of classical trajectories are in good qualitative agreement with full quantum mechanical calculations.

There were no patents under Award F49620 - AFOSR 86-0006.

Very truly yours,

Stuart A. Rice

Stuart A. Rice
Frank P. Hixon Distinguished Service
Professor of Chemistry

cc: J. Trubatch
R. Szara

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